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## Centrifugally Cast Glass-Ceramic Pipe From Mining and Processing Wastes

By Arthur V. Petty, Jr.



UNITED STATES DEPARTMENT OF THE INTERIOR

**Report of Investigations 8910**

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**UNITED STATES DEPARTMENT OF THE INTERIOR**

**William P. Clark, Secretary**

**BUREAU OF MINES**

**Robert C. Horton, Director**

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## CONTENTS

	<u>Page</u>
Abstract.....	1
Introduction.....	2
Acknowledgment.....	3
Utilization of mining and processing waste by the ceramic industry.....	3
Centrifugal casting equipment and process.....	5
Centrifugally cast glass-ceramic pipe from mining and processing wastes.....	8
Summary and conclusions.....	12
References.....	14
Appendix A.--Mining and processing wastes.....	16
Appendix B.--Centrifugal casting process.....	18
Appendix C.--Computer program to optimize mixes of waste materials for glass-ceramic compositions.....	21

## ILLUSTRATIONS

1. Centrifugal casting apparatus used to produce glass-ceramic pipe.....	6
2. Pouring molten glass into preheated, rotating mold using mechanical tongs	7
3. Elevated furnace used to melt glass and direct it into preheated, rotating mold below.....	7
4. Centrifugally cast glass pipe and test disks.....	8
5. Location of glass-ceramic compositional areas within the $MgO-Al_2O_3-SiO_2$ phase diagram.....	9
6. Location of glass-ceramic compositional areas within the $Na_2O-Al_2O_3-SiO_2$ phase diagram.....	9
7. Location of glass-ceramic compositional areas within the $FeO-Al_2O_3-SiO_2$ phase diagram.....	9
8. Location of glass-ceramic compositional areas within the $CaO-Al_2O_3-SiO_2$ phase diagram.....	9
9. Location of glass-ceramic compositional areas within the $CaO-MgO-SiO_2$ phase diagram.....	10
10. Scanning electron micrograph of glass-ceramics produced from slate waste.	13
11. Scanning electron micrograph of glass-ceramics produced from copper mine tailings.....	14
B-1. Stress element for centrifugal casting.....	18

## TABLES

1. Current and potential utilization of waste materials by the ceramic industry.....	4
2. Typical oxide compositions of various waste materials.....	5
3. Chemical composition and mineralogy of waste materials.....	11
4. Oxide composition of glasses produced from slate waste and copper mill tailings.....	12
5. Taber wear index for glass-ceramics produced from slate and copper mill tailings and related values for other alumina-containing ceramics.....	12
A-1. Amounts of major mining wastes.....	16



# UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	μm	micrometer
ft	foot	P	poise
ft/s <sup>2</sup>	foot per second squared	pct	percent
h	hour	psi	pound per square inch
in	inch	rpm	revolution per minute
lb	pound	s	second
lbf	pound (force)	vol pct	volume percent
lbf/in <sup>2</sup>	pound (force) per square inch	wt pct	weight percent
lbf/in <sup>3</sup>	pound (force) per cubic inch	yr	year
min	minute		

# CENTRIFUGALLY CAST GLASS-CERAMIC PIPE FROM MINING AND PROCESSING WASTES

By Arthur V. Petty, Jr.

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## ABSTRACT

The Bureau of Mines has researched the utilization of mining and processing wastes as raw materials for the production of glass-ceramic pipe. Characterization of various wastes as to occurrence and chemical composition is reported. A computer program was developed and used to identify waste materials and mixes that would result in glass melts from which glass-ceramics could be produced after cooling and subsequent heat treatments. The production of abrasion-resistant pipe from inexpensive and readily available domestic resources could offer an economical substitute for high-alloy steels containing the critical and strategic materials cobalt and chromium.

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## INTRODUCTION

Glass-ceramic pipe potentially can replace abrasion- and wear-resistant alloys requiring critical and strategic raw materials such as cobalt, nickel, and chrome. Potentially, glass melts can be made from wastes and other abundant, low-cost, domestic raw materials, which after cooling and subsequent heat treatments could produce a glass-ceramic.

In evaluating the present and potential utilization of waste materials to produce glass-ceramic pipe, consideration must be given to the various types of wastes available in the United States. This includes both the present and projected production rates, the availability of stockpiles, the location of sources and stockpiles relative to market areas, other potential uses outside the ceramic industry, which could compete for wastes, the costs of recovering and upgrading (where required) waste materials to make them competitive with natural mineral raw materials, and perhaps most importantly, the chemical compositions of wastes relative to the basic raw material needed to produce a glass-ceramic pipe.

Over 3 billion tons of mining, industrial, agricultural, and municipal wastes are generated annually in the United States (1).<sup>2</sup> More than 70 pct of this amount comes from mining operations in the form of waste rock, mill tailings, and coal refuse, which are being added to some 23 billion tons of mining waste already accumulated. Production of many of the wastes is expected to grow steadily, and production of others may grow at alarming rates. For example, because of the recent emphasis on coal utilization, the waste piles of coal refuse and fly ash and waste ponds of sulfate sludges could grow rapidly. The commercialization of developing technologies for energy production and for protection of the environment could also result in the

generation of substantial amounts of processing and mineral wastes.

Most of the wastes are disposed of by being placed in settling ponds and containment dikes or by being used as land-fill materials. Only a small amount of most wastes is being used for construction purposes. An exception is slags, which are being used extensively as aggregate. In several other cases, construction materials that are at least the technical equivalent of materials produced from virgin resources have been produced from wastes.

Several factors have impeded the large-scale use of wastes, including the abundant supply of natural resources, the abundant supply and low cost of energy for processing natural resources, the low cost of disposing of wastes, lack of adequate technical information on the performance of materials produced from wastes, and lack of appropriate standards and specifications for materials produced from wastes. However, during the past decade significant programs that should facilitate the increased use of waste materials have been established in the United States.

For example, the feasibility of using waste materials as sources of aggregate has been explored in projects sponsored by the Federal Highway Administration; the U.S. Department of Energy has supported work relating to the conservation of energy by substituting waste materials for more energy-intensive materials; the U.S. Environmental Protection Agency has supported demonstrations of uses of waste materials as an approach to improve the Nation's environment; and the Bureau of Mines has investigated a number of uses for mineral wastes. In addition, the Resource Conservation Act of 1976 (Public Law 94-580) was intended to encourage the increased use of waste materials.

Other important activities in the United States that have stimulated

<sup>2</sup>Underlined numbers in parentheses refer to items in the list of references preceding the appendixes.

interest in the use of waste materials include the Mineral Waste Utilization Symposia,<sup>3</sup> the Ash Utilization Symposia,<sup>4</sup> and the work of the E-38 Committee on Resource Recovery of the American Society for Testing and Materials (ASTM). Within the committee, the E38.06 subcommittee was specifically established to cover "Materials of Construction From Other Recovered Materials."

Regional material and energy shortages are providing growing incentives for the increased use of waste materials. Ultimately, the amount of waste materials used in construction will depend on the development of economic incentives, either formed in the marketplace or created by governmental policies.

#### ACKNOWLEDGMENT

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This report presents uses of mining and process wastes by the ceramic industry and research at the Bureau's Tuscaloosa Research Center on the centrifugal casting of glass-ceramic pipe. Results are given on the properties of glass-ceramic materials produced from slate and serpentine mining wastes and copper mill tailings. The report also includes a review of various mining, processing, and municipal wastes (appendix A) and a review of the centrifugal casting of metal, concrete, and molten rock (appendix B). A sample output of the computer program developed and used as an aid to optimize glass-ceramic compositions from wastes is included as appendix C.

Alabama, for the development of the computer program.

#### UTILIZATION OF MINING AND PROCESSING WASTE BY THE CERAMIC INDUSTRY

Table 1 summarizes current and potential utilization of waste materials by various sectors of the ceramic industry. In addition, there are other small-scale applications, usually dictated by localized lack of raw materials; for example, specialized products have been developed to utilize a particular waste material where suitable disposal by other means is impractical, and individual companies have developed products to utilize their own waste materials.

As noted in the introduction, utilization of wastes has been low in the United States for a variety of reasons; however, the chemical composition of many wastes, as shown in table 2, makes them suitable

for use by the ceramic industry. In many cases the technology is partially available, but in all probability economic incentives, governmental regulations, or pressure from the general public will be required to induce producers to more fully utilize waste materials.

Published research indicates numerous potential applications of waste materials in the production of ceramic products, including lightweight aggregate and other structural clay products. The production of highway aggregate having high skid and wear resistance offers high-tonnage usage of a variety of wastes, often close to the source. Blown or spun glass fibers for insulation and the development of pozzolanic compositions to reduce the demand for portland cement offer two other alternatives.

The area of waste utilization offering the greatest potential is in the development of glass-ceramic compositions, where the waste is melted to form a glass, fabricated using conventional glass-forming techniques, and subsequently

<sup>3</sup>Biennial symposia held between 1968 and 1980, cosponsored by the Bureau and the Illinois Institute of Technology Research Institute (IITRI).

<sup>4</sup>Triennial symposia held since 1967, sponsored jointly by the National Coal Association, Edison Electric Institute, American Public Power Association, National Ash Association, and the Bureau.

TABLE 1. - Current and potential utilization of waste materials by the ceramic industry

<u>Waste material</u>	<u>Utilization</u>
Alumina red and brown muds.....	Insulation.
Asbestos (mining).....	Ceramic tile, refractory brick.
Blast furnace (air cooled).....	Mineral wool, roof.
Blast furnace (all types).....	Aggregate.
Blast furnace (expanded).....	Cement manufacture.
Blast furnace (granulated).....	Do.
Cement kiln dust.....	Cements.
Coal refuse.....	Aggregate.
Converter.....	Do.
Copper industry (mining and milling).....	Brick.
Copper slag.....	Cement.
Feldspar (mining).....	Brick, lightweight aggregate.
Fluorspar (mining).....	Aggregate.
Fly ash, boiler slag, and bottom ash.....	Portland cement, lightweight aggregate.
Foundry waste.....	Fine aggregate.
Gold industry (mining and milling).....	Brick.
Gypsum (mining).....	Do.
Iron ore .....	Concrete aggregate.
Lead (mining and milling).....	Refractory brick.
Mud residues from aluminum extraction.....	Ceramic foam, cement, lightweight aggregate.
Municipal waste glass.....	Cullet, structural clay products, lightweight aggregate, glassphalt, glass wool.
Oil shale.....	Lightweight aggregate.
Phosphate slag.....	Lightweight aggregate, ceramic tile, cement.
Phosphate slime.....	Lightweight aggregate, brick, pipe.
Slate (mining).....	Lightweight aggregate.
Taconite.....	Concrete aggregate, skid-resistant aggregate, building block.
Zinc (mining and milling).....	Refractory brick.
Zinc smelter slag.....	Fine aggregate.

nucleated and devitrified in a controlled manner through heat treatment. The resultant, partially crystallized material offers improved strength and chemical and abrasion resistance. Applications for these glass-ceramic materials would include structural products, pipe or pipelins to transport abrasive or corrosive fluids, alkali-resistant fibers to replace asbestos in concrete products, and use as a matrix material in which radioactive wastes could be chemically incorporated in a stable, nonleachable, solid form. Specific advantages in using these materials include the following:

1. Glass-ceramic products offer greater strength and improved resistance to mechanical abrasion and chemical corrosion over other materials, at relatively low cost. In many cases these products could be used to replace stainless steel alloys containing such critical materials as chromium, nickel, and cobalt.

2. Valuable trace elements or metals may be recovered during the melting of waste materials to form glass compositions.

TABLE 2. - Typical oxide compositions of various waste materials, percent

Waste	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Other
Anthracite coal refuse.	50-57	30 -37	3 -10	1 -2	0 - 1	TiO <sub>2</sub> , MnO.
Anthracite fly ash	50-57	30 -37	3 -10	1 -2	0 - 1	TiO <sub>2</sub> , Na <sub>2</sub> O, K <sub>2</sub> O.
Bituminous coal refuse.	50-61	16 -28	6 -21	0 -2	0 - 2	NAp.
Bituminous fly ash	34-52	13 -31	6 -25	1 -12	.5- 3	C, Na <sub>2</sub> O, SO <sub>3</sub> .
Blast furnace slag	33-42	.3- 2	1.5- 5.1	36 -45	3 -16	NAp.
BOF steel slag....	21.7	16.3	3.8	40.3	4.4	NAp.
Boiler slag.....	42.7	27.5	21	6.4	1.1	TiO <sub>2</sub> .
Bottom ash.....	20-60	10 -35	5 -35	1 -20	.3- 4	Na <sub>2</sub> O, K <sub>2</sub> O.
Brown mud.....	23.3	6.4	6.1	46.6	NAp	P <sub>2</sub> O <sub>5</sub> .
Cement kiln dust..	11.1	.5	2.9	44	2.5	TiO <sub>2</sub> , Na <sub>2</sub> O, K <sub>2</sub> O.
Converter slag....	25.6	6.7	18	25.1	10.6	MnO.
Copper slag.....	36	8	52	6	NAp	NAp.
Copper tailings...	71.1	13.2	4.9	1.1	2.1	Na <sub>2</sub> O, K <sub>2</sub> O.
Ferromolybdenum slag.	37	36	23.7	1.9	1	NAp.
Foundry slag.....	33.3	18.2	11.1	40.9	3.8	NAp.
Gold tailings.....	93	3.5	1.9	1	.41	NAp.
Lead slag.....	22.8	NAp	40.6	9.8	4.4	NAp.
Lead-zinc tailings	9.8	.3	1	29.5	17.8	Na <sub>2</sub> O, TiO <sub>2</sub> .
Lignite fly ash...	15-52	8 -25	2 -19	11 -36	2 -11	C, Na <sub>2</sub> O, SO <sub>3</sub> .
Municipal incinerator residue.	53-57	3.7- 8.2	9.5-14.4	4.3-62	1.5- 2.8	Wood, plastic, metal, other organics.
Nickel slag.....	53.3	1.5	11	.6	30.1	MnO.
Open hearth slag..	18-26	6.7- 8.5	18	25 -36	10	NAp.
Phosphate slag....	44.8	6.2	1.6	41.7	.8	Na <sub>2</sub> O, fluorides.
Phosphate slime...	31-46	6 -18	3 - 7	14 -23	1 - 2	Na <sub>2</sub> O, K <sub>2</sub> O, SO <sub>2</sub> .
Red mud.....	22.9	26.5	10.7	8.1	NAp	Na <sub>2</sub> O, TiO <sub>2</sub> .
Taconite tailings.	59	2.7	21	2.7	3.7	Na <sub>2</sub> O, K <sub>2</sub> O.
Tin slag.....	23	15	13.6	5	11	Heavy metals.
Zinc slag.....	30	NAp	22.6	6.5	NAp	NAp.

NAp Not applicable.

3. Less energy is required in producing glass-ceramics from waste materials than in producing them from other beneficiated and processed raw materials.

4. Large or complex shapes can be produced economically, since glass-ceramics are fabricated using conventional glass-forming techniques.

5. A wide variety of waste materials can be utilized in the development of glass-ceramic compositions.

6. Since the wastes are melted in forming glass-ceramic materials, many wastes that could not otherwise be used because of environmental restrictions can be utilized, and hazardous waste can be removed.

#### CENTRIFUGAL CASTING EQUIPMENT AND PROCESS

The centrifugal casting apparatus is shown in figure 1. A preheated delivery chute is used to channel the molten glass

into a rotating (also preheated) mold. The mold is mounted on a drive spindle, which is connected to a variable-speed



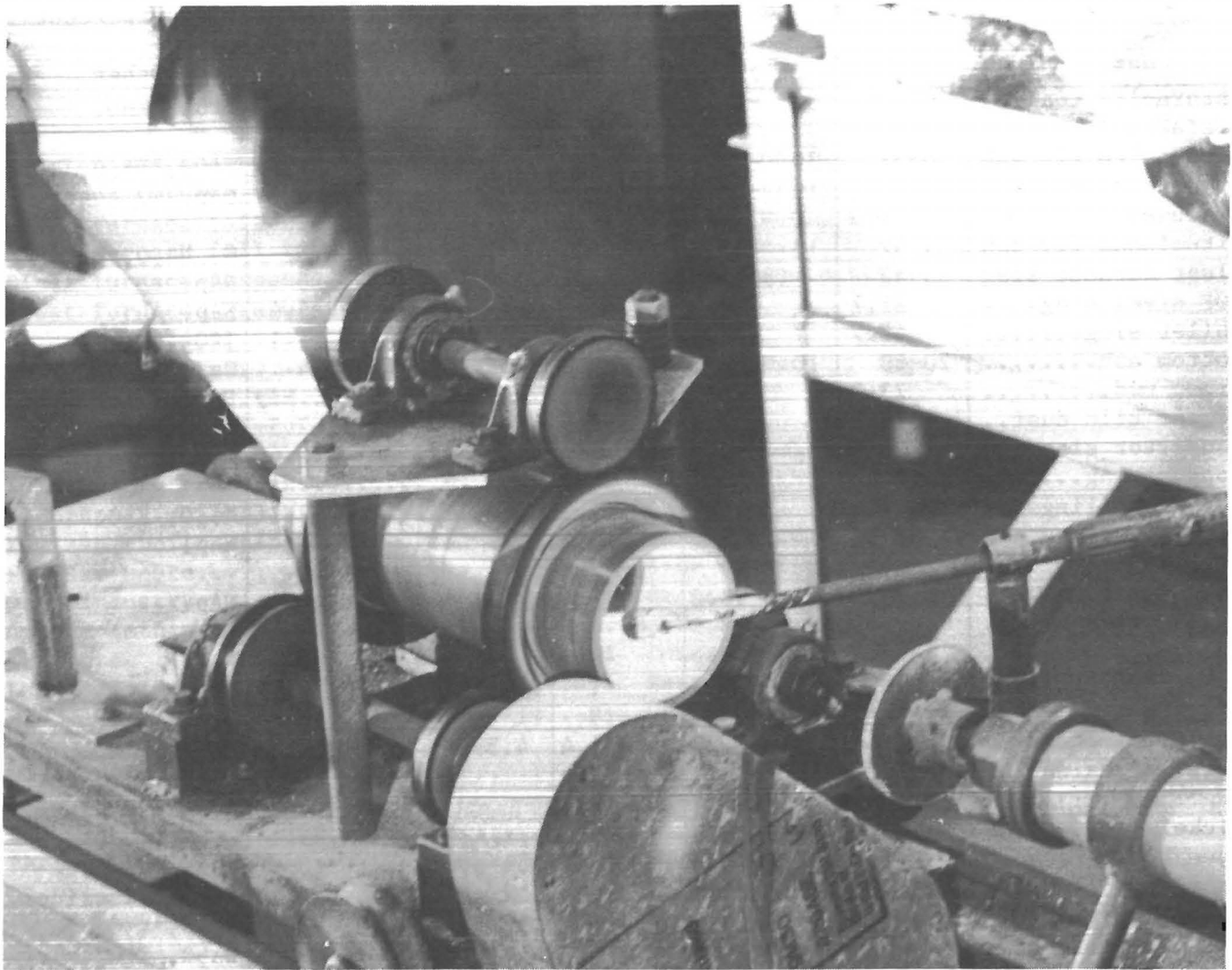


FIGURE 1. - Centrifugal casting apparatus used to produce glass-ceramic pipe.

motor. The entire mold assembly is mounted on a horizontal track and can be moved back and forth by another variable-speed motor. A pneumatic ram is positioned horizontally along the axis of mold rotation and is used to eject the centrifugally cast pipe from the mold. The mold is lined with a ceramic fiber material to allow for differences in thermal expansion of the mold and glass pipe. Rings are friction-fit into each end of the mold to prevent molten glass from being slung out of the mold.

Initially, glass batches were melted in a crucible, removed from the furnace with mechanical tongs, and poured into the delivery chute (fig. 2). This resulted in poor inside surfaces of the cast piece

because pieces of a crust-like surface broke loose during pouring and flowed into the mold. To avoid this problem, an elevated furnace was built as shown schematically in figure 3. A 5/8-in hole was drilled in the bottom of the crucible and plugged with a graphite cone attached to a silicon carbide rod. The batch was melted, the plug was removed, and molten glass flowed through the hole in the crucible into the delivery chute positioned directly below it. This allowed the crusty material to remain in the crucible and resulted in bubble-free, homogeneous glass flowing into the mold.

Typically, a batch of the various raw materials, weighing 5 to 8 lb, was dry-mixed and loaded into the crucible. The

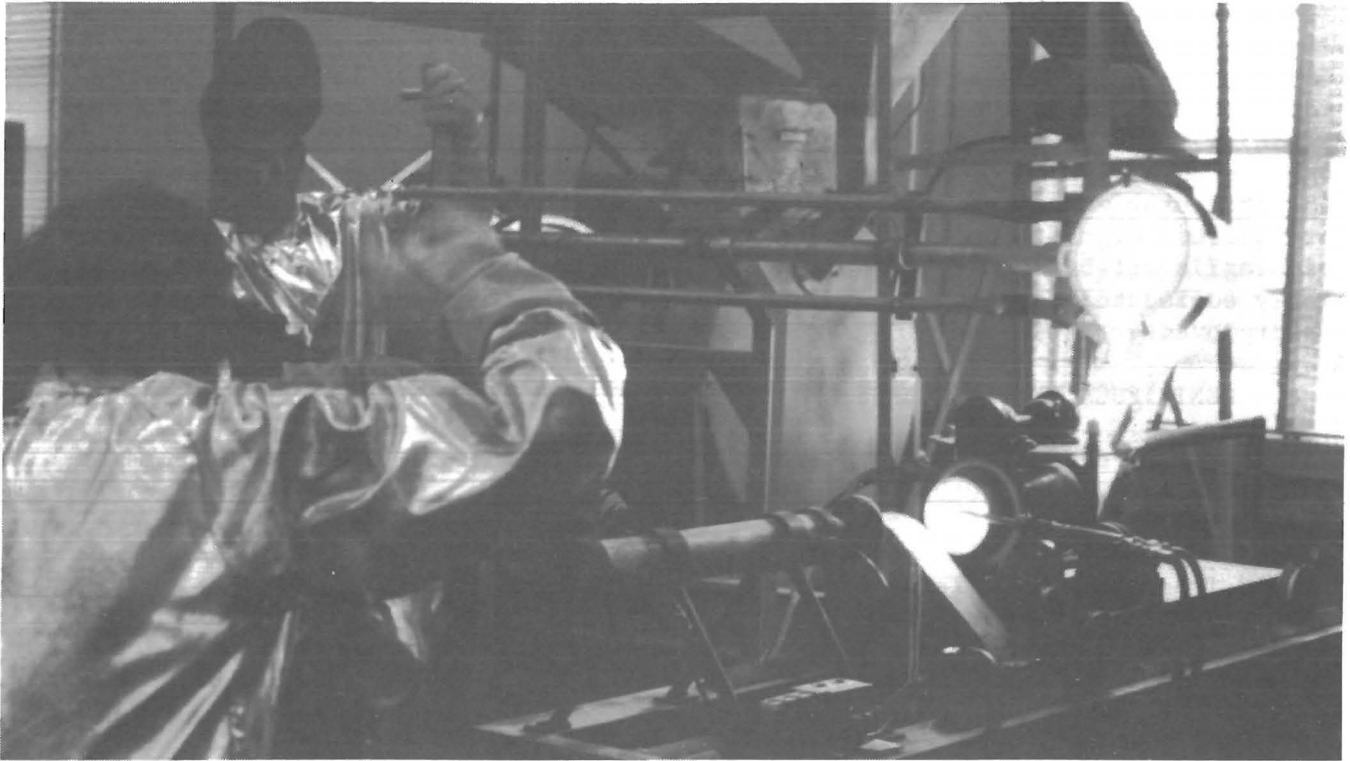


FIGURE 2. - Pouring molten glass into preheated, rotating mold using mechanical tongs.

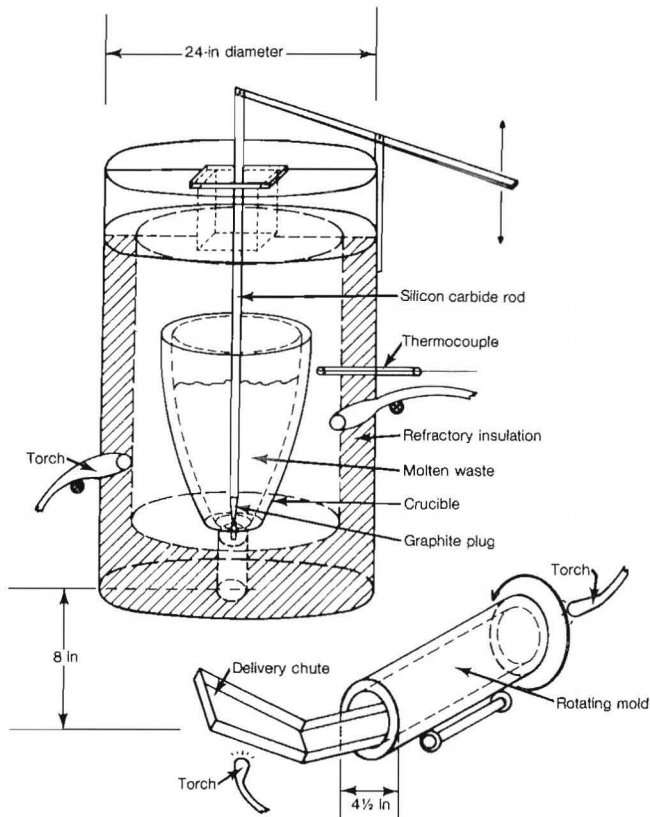


FIGURE 3. - Elevated furnace used to melt glass and direct it into preheated, rotating mold below.

temperature was slowly raised to approximately  $1,000^{\circ}\text{C}$  and held there sufficiently long to allow decomposition of the carbonates. (Failure to do this resulted in extreme foaming in the molten glass.) Following this, the temperature was increased to approximately  $1,500^{\circ}\text{C}$  and held there for 2 to 4 h to ensure homogeneity of the melt. The delivery chute and mold were preheated, using oxy-propane torches, to about  $900^{\circ}\text{C}$ .

The plug was then raised, allowing molten glass to flow from the crucible, down the chute, and into the rotating mold. A rotational speed of approximately 650 rpm was shown to provide adequate centrifugal force to keep molten glass in contact with the mold's inner surface. When sufficient glass had entered the mold, the plug was lowered to stop the flow, the torch used to preheat the chute was extinguished, and the rotating mold was moved horizontally to allow the glass to be rotated out of the way. The torch used to preheat the mold was left on to allow the glass to spread uniformly through the mold; then it was extinguished and removed. When the pipe



had cooled sufficiently to support its own weight, the horizontal movement of the mold was locked and the rotation stopped. The cast pipe section, measuring 3-3/4 in. in outside diam by 10 in long, with a uniform wall thickness of 1/8 to 1/2 in, was ejected and placed in an annealing oven at 650° C. After again reaching equilibrium, the furnace was slowly cooled to room temperature and the pipe removed.

Following this, the pipe sections were heated to 720° to 750° C and held for 2 to 8 h to initiate nucleation, then raised in temperature to 930° to 1,000° C to allow crystal growth. Disk-shaped pieces of each composition were prepared and heat-treated according to the same schedules as the pipe and used for evaluation. Figure 4 shows glass and glass-ceramic pipe and disks.

#### CENTRIFUGALLY CAST GLASS-CERAMIC PIPE FROM MINING AND PROCESSING WASTES

In surveying over 100 articles from the literature and over 300 U.S. and foreign patents, it was found that glass-ceramic compositions that could potentially be derived from waste materials fall within one of five ternary phase diagrams:

1.  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ ,
2.  $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ ,
3.  $\text{FeO-Al}_2\text{O}_3\text{-SiO}_2$ ,

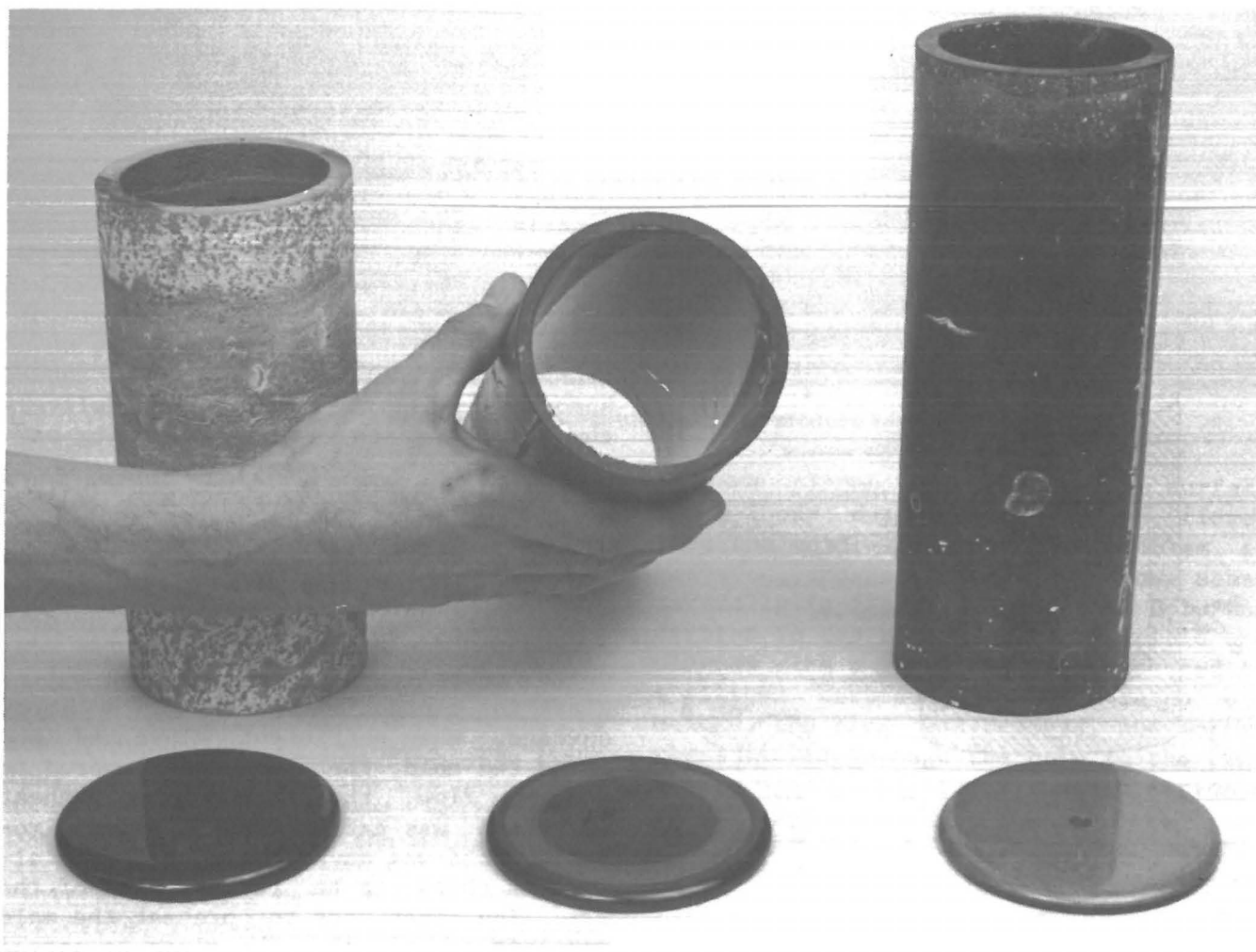


FIGURE 4. - Centrifugally cast glass pipe and test disks.

4.  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ ,

5.  $\text{CaO-MgO-SiO}_2$ .

The compositional areas cited in the literature are shown graphically in figures 5 through 9. The  $\text{CaO-MgO-SiO}_2$  system is most promising for the utilization of a variety of waste materials. Comparing table 2 with figure 9 shows that most of the waste materials fall generally within

this system. The literature also highlights this particular system, as indicated by the numerous references (2-6). The primary areas of interest within this ternary system are centered around a composition of 55 pct  $\text{SiO}_2$ , 18 pct  $\text{MgO}$ , and 27 pct  $\text{CaO}$ , and yield crystalline phases of diopside ( $\text{CaO}\cdot\text{MgO}\cdot 2\text{SiO}_2$ ), pseudowollastonite ( $\alpha\text{-CaO}\cdot\text{SiO}_2$ ), wollastonite ( $\beta\text{-(Ca, Mg)O}\cdot\text{SiO}_2$ ), and forsterite ( $2(\text{Mg, Ca})\text{O}\cdot\text{SiO}_2$ ). The structure of these

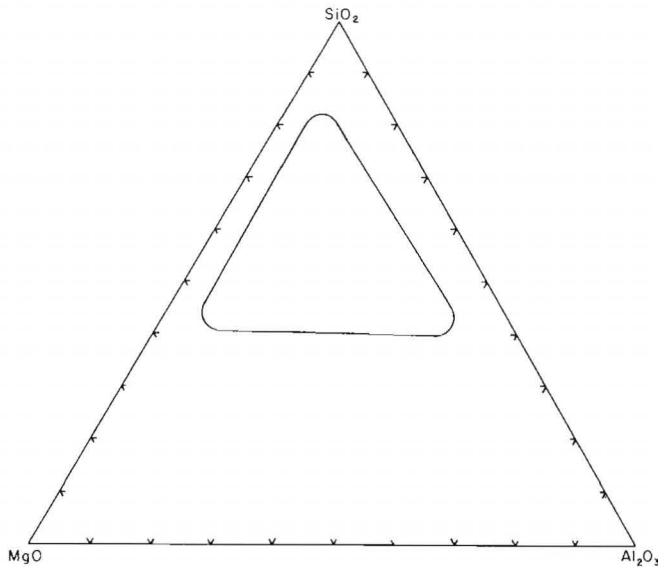


FIGURE 5. - Location of glass-ceramic compositional areas within the  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$  phase diagram.

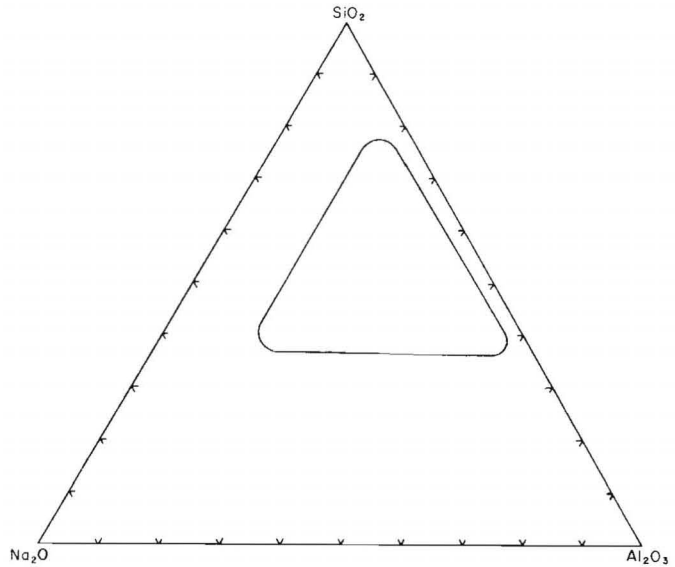


FIGURE 6. - Location of glass-ceramic compositional areas within the  $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$  phase diagram.

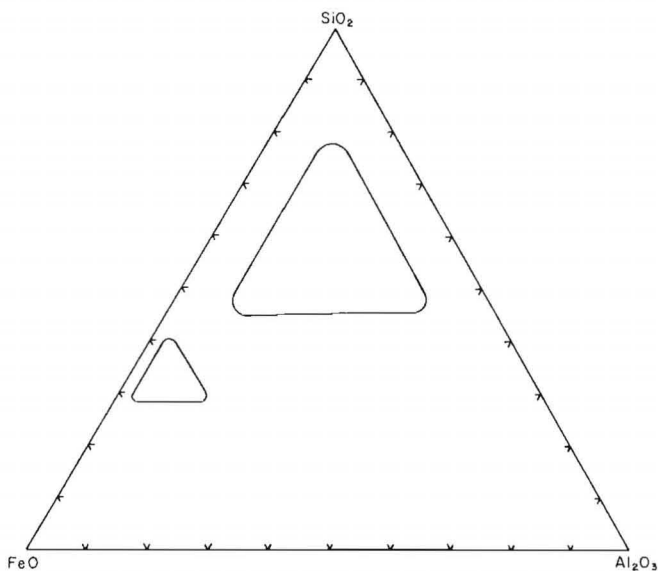


FIGURE 7. - Location of glass-ceramic compositional areas within the  $\text{FeO-Al}_2\text{O}_3\text{-SiO}_2$  phase diagram.

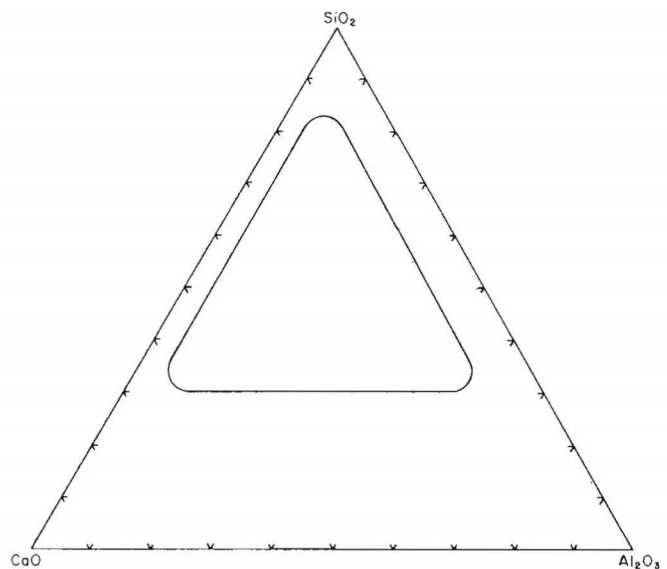


FIGURE 8. - Location of glass-ceramic compositional areas within the  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$  phase diagram.

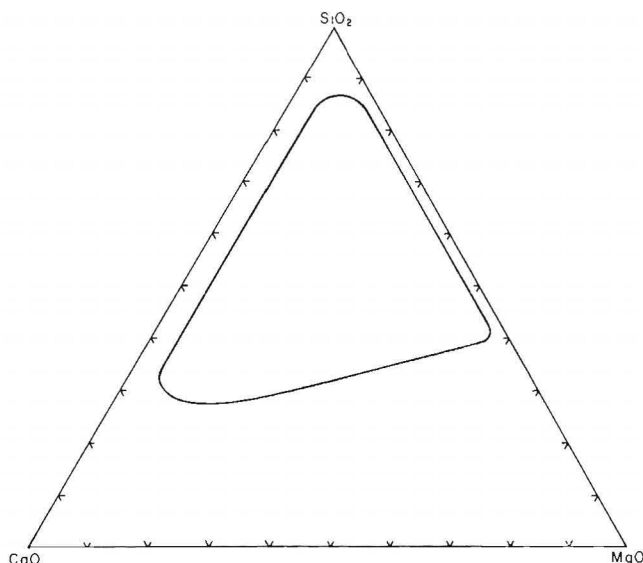


FIGURE 9. - Location of glass-ceramic compositional areas within the  $\text{CaO-MgO-SiO}_2$  phase diagram.

phases can also accommodate large amounts of a variety of impurity oxides. The majority of the waste materials shown in table 1 can be adjusted to this composition by the addition of abundant, low-cost raw materials including silica sand, limestone ( $\text{CaCO}_3$ ), and dolomite ( $\text{Ca} \cdot \text{MgCO}_3$ ). The presence of iron in many of the wastes poses no problem since significant amounts of iron can be accommodated into both the diopside and pseudowollastonite structures.

An interactive computer program, written in BASIC, was developed and used to determine optimum mixtures of available waste materials and/or other low-cost raw materials and minor additions made to lower viscosity and/or promote nucleation. The menu-operated program gives the user several options, including

1. Specification of the optimum mixing of two or more wastes listed in the data bank and/or other raw material compositions input from the keyboard to achieve a desired composition.

2. A search of the data bank to select the "most suitable" waste composition to use to obtain a desired composition, while minimizing other raw material additions.

3. A search of the data bank to identify materials having desired "oxide-equivalent" contents.

This program operates with a data base that presently contains information on 32 waste products and their typical oxide-equivalent compositions. The oxides included in the data base are  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ , and  $\text{MgO}$ . Up to three additional oxides of interest can be handled by the program. The program allows for the combination of any waste, either from the data base or user specified, with up to two additional wastes and any or all of the raw materials sand, dolomite, and calcium carbonate. The program is menu driven and prompts the user for input data. The options available are to specify the best combination of raw materials and chosen wastes or to select suitable wastes to use, given the desired combination. The criterion for selection is a least squares minimization of the deviation from a desired composition. A sample of the program listing and sample output for slate mining waste is given in appendix C.

Three waste materials that represented a wide range of composition and mineralogical makeup, as shown in table 3, were selected to produce glass-ceramic pipe. These materials were serpentine and slate mining wastes and copper mill tailings. The serpentine waste (from an asbestos mine) was also chosen because producing a glass product from these wastes would eliminate a potential environmental health hazard.

Initial studies, using the slate waste and copper mill tailings, were made to optimize melt compositions. Primary considerations were (1) the melting point of the batch, (2) the viscosity of the melt, (3) working range, and (4) the ability to heat-treat the melt to produce homogeneous bulk nucleation and crystallization. With the aid of the computer program, compositions were selected in an area of the  $\text{CaO-MgO-SiO}_2$  phase diagram near the diopside ( $\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$ ) phase area. In the case of the slate waste, this involved the addition of dolomite and

TABLE 3. - Chemical composition and mineralogy of waste materials, percent

Waste	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	Fe	Alkali	Mineral phases
Copper mill tailings.	67.6	11.2	2.6	2.9	2.7	6.4	Quartz, orthoclase, mica, plagioclase, <sup>1</sup> pyrite. <sup>1</sup>
Serpentine....	40.4	.61	.13	39.6	5.0	ND	Serpentine, magnetite, <sup>1</sup> calcite. <sup>1</sup>
Slate waste...	61.7	16.2	.6	.8	4.9	4.15	Quartz, chlorite, mica, <sup>1</sup> calcite, <sup>1</sup> plagioclase.

ND Not determined. <sup>1</sup>Minor phases.

limestone, while in the case of copper mill tailings, additions of dolomite and MgO were required. Varying the ratio of SiO<sub>2</sub> to CaO resulted in changes in viscosity (fluidity) of the melt. Based on preliminary small-scale tests, a SiO<sub>2</sub>:CaO ratio of 1.5 to 3.5 was selected.

Alkalies present in the waste materials serve to flux the glass during initial melting and thus lower the viscosity. Compositions involving the addition of alkali (in the form of sodium borate or sodium carbonate) showed that alkali additions improved the fluidity of the melt and extended the working range. Optimum results were obtained with alkali contents ranging from 5 to 7.5 pct. After nucleation and devitrification, the alkali is partially contained in the diopside structure, may or may not form minor amounts of nepheline (Na<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>), or remains in the glassy phase.

Varying the MgO content of the glass from 10 to 20 pct resulted in significant viscosity changes and in the ability to achieve controlled nucleation and devitrification. Increasing the MgO content above 15 pct caused increased fluidity but led to spontaneous and uncontrolled devitrification during heat treatment. MgO contents of 12 to 15 pct were selected. Aluminum in the waste materials is incorporated into the diopside structure or occurs in minor amounts of gehlenite (2CaO·Al<sub>2</sub>O<sub>3</sub>·SiO<sub>2</sub>) and/or fayalite (2FeO·SiO<sub>2</sub>).

Iron occurring in the wastes can generally be accommodated into the diopside and pseudowollastonite structures. Excess iron nucleates as γ-Fe<sub>2</sub>O<sub>3</sub> and

serves as a promoter for bulk crystallization. It was noted that melts produced in gas-fired furnaces were more fluid than those produced in electric furnaces. This was shown to result from the valence state of the iron. Samples fired in a gas-fired furnace in which a reducing atmosphere was present contained a higher ratio of Fe<sup>+2</sup> to Fe<sup>+3</sup> than those fired in an electric furnace with a slightly oxidizing atmosphere. The increased fluidity could be obtained in an electric furnace atmosphere by adding 4 pct powdered charcoal to the batch. The presence of Fe<sup>+2</sup> resulted in better bulk crystallation.

Additions of chromite and titania (TiO<sub>2</sub>) were also made to the glass melts to determine their effect on bulk crystallation. TiO<sub>2</sub> seemed to have no effect, while chromite additions ranging from 2 to 5 wt pct greatly improved bulk crystallation. Domestic chrome ore was used to supply the Cr<sub>2</sub>O<sub>3</sub>.

Initial work with the serpentine waste involved additions of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> to produce a batch containing 54 pct SiO<sub>2</sub>, 23 pct Al<sub>2</sub>O<sub>3</sub>, and 23 pct MgO. It was hoped that this composition would produce a melt from which cordierite (2MgO·2Al<sub>2</sub>O<sub>3</sub>·5SiO<sub>2</sub>) could be crystallized. Inability to produce controlled devitrification of this composition led to a recalculation of batch composition in which SiO<sub>2</sub> and CaO were added to produce a diopside crystalline phase. Although a crystalline glass-ceramic was produced from this composition, no further work was attempted since the serpentine waste accounted for only 25 wt pct of the diopside (CaO·MgO·2SiO<sub>2</sub>) composition.

The final compositions of batches based on slate waste and copper mill tailings, which were used to produce centrifugally cast glass-ceramic pipe, are shown in table 4. Viscosities of the glass melts ranged from 40 to 80 P at 1,500° C.

TABLE 4. - Oxide composition of glasses produced from slate waste and copper mill tailings, percent

Oxide	Glass 1 <sup>1</sup>	Glass 2 <sup>2</sup>
Al <sub>2</sub> O <sub>3</sub> .....	11.3	8.8
Alkali.....	4.0	5.7
CaO.....	23.3	15.0
Cr <sub>2</sub> O <sub>3</sub> .....	1.6	1.3
FeO.....	4.2	3.6
MgO.....	12.1	15.3
SiO <sub>2</sub> .....	40.1	50.2
SiO <sub>2</sub> :CaO ratio.....	1.7	3.3

<sup>1</sup>Based on slate waste (60 pct by weight of batch).

<sup>2</sup>Based on copper mill tailings (55 pct by weight of batch).

X-ray diffraction showed the crystalline phase in glass-ceramics produced from slate waste to be principally diopside, with minor amounts of wollastonite and gehlenite. Using calibrated standards, X-ray diffraction also indicated the material to be approximately 85 pct crystalline and 15 pct amorphous. This is substantiated by the scanning electron micrograph shown in figure 10. Average crystalline size was determined to be 1 to 2  $\mu$ m. The micrograph, typical of polished and etched fracture surfaces, indicates extremely uniform grain size and

distribution. Densities for the starting glass and heat-treated glass-ceramic were 2.668 and 2.754, respectively, indicating a 3-vol-pct change during crystallization. Contact abrasion was measured using the Taber Abrasion Tester, ASTM C501 (7). The results, summarized in table 5, indicate that the abrasion resistance falls between that of the 45- and 83-pct-Al<sub>2</sub>O<sub>3</sub> materials.

Glass-ceramics produced from copper mill tailings were primarily diopside in a glassy matrix. The crystals were somewhat larger (averaging 5  $\mu$ m), less uniform, and represent about 65 vol pct of the solid. A typical micrograph is shown in figure 11. Densities for the glass and glass-ceramic were 2.603 and 2.672, again indicating minimal volume change. Table 5 indicates similar, but slightly higher values than those obtained for the glass-ceramics produced from slate waste.

TABLE 5. - Taber wear index for glass-ceramics produced from slate and copper mill tailings and related values for other alumina-containing ceramics

Sample	Index
38 pct Al <sub>2</sub> O <sub>3</sub> .....	27,000
45 pct Al <sub>2</sub> O <sub>3</sub> .....	10,300
Glass-ceramics:	
Copper mill tailings.....	998
Slate waste.....	876
83 pct Al <sub>2</sub> O <sub>3</sub> .....	156
96 pct Al <sub>2</sub> O <sub>3</sub> .....	16.8

## SUMMARY AND CONCLUSIONS

In a summary of the literature on centrifugal casting (appendix B), several factors emerge as guiding principles in the design of a successful system: (1) The raw feed materials must possess a controllable viscosity or working range, (2) the feed rate and method of introducing feed to the centrifugal mold is critical, (3) the rotational speed of the mold must be optimized and controlled so

as to cause uniform distribution of feed within the mold and to densify the formed piece, (4) the use of different rotational speeds for mold loading and densification is often required, and (5) the most important periods in producing centrifugally cast glass-ceramic pipe are the annealing, nucleation, and crystallization temperature-time cycles.



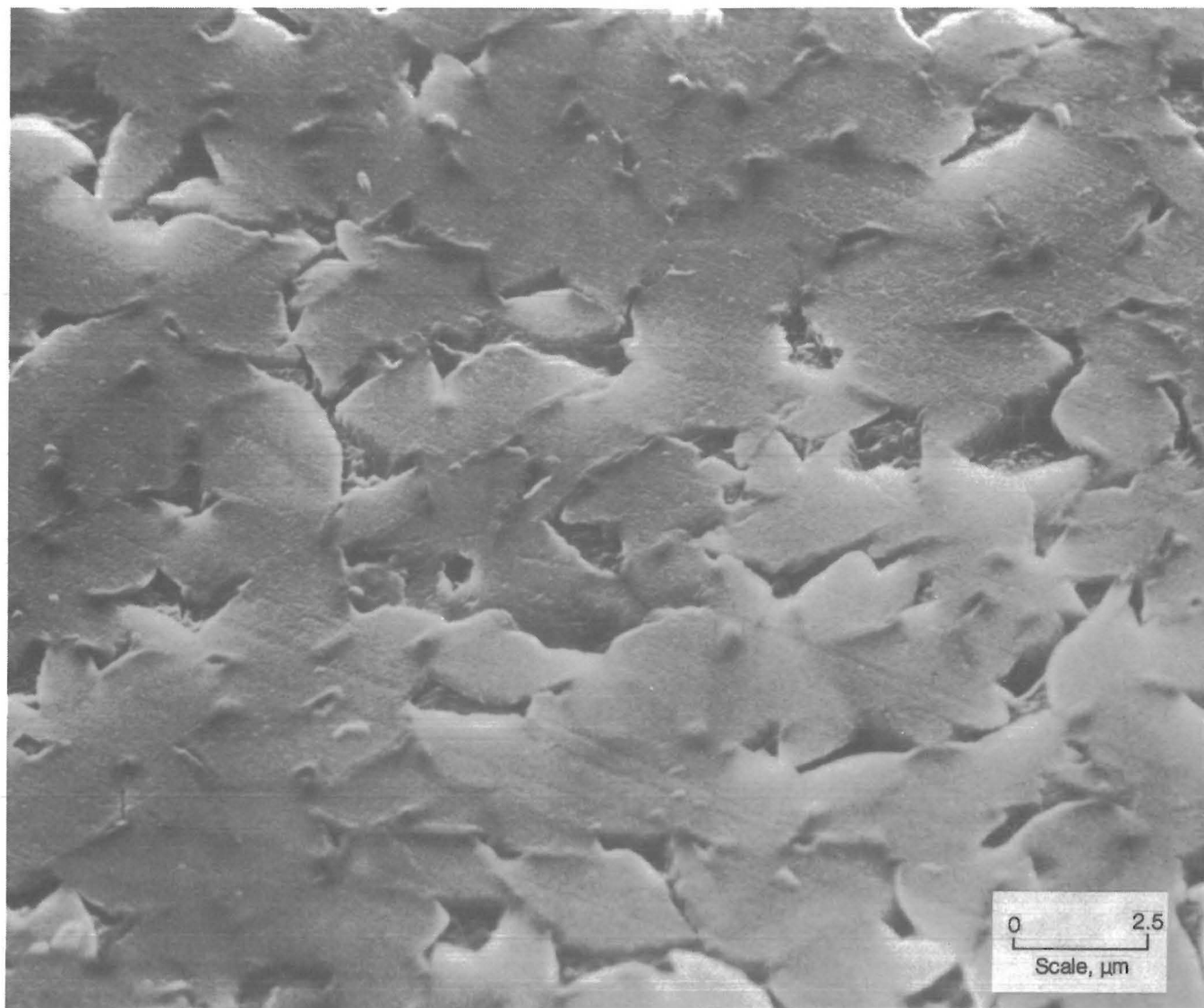


FIGURE 10. - Scanning electron micrograph of glass-ceramics produced from slate waste.

Equipment was designed and constructed by the Bureau of Mines to allow melting of 6- to 12-lb glass batches, and subsequent centrifugal casting of 3-3/4-in-diam pipe, 10 in long, from the melt. Appropriate selection of the starting batch composition allows heat treatment of the pipe, after cooling, to produce controlled nucleation and devitrification. The resulting glass-ceramic pipe, because of its homogeneous crystalline structure composed of uniformly sized crystallites, offers unique properties.

The glass batches used in the investigation were primarily composed of waste materials. Slate waste, copper

mill tailings, and serpentine (asbestos waste) were used with other low-cost, abundant raw materials to produce glass-ceramics composed of diopside. A computer program was written, which presently contains a data base of 32 waste materials, and was used to optimize particular batch compositions from available wastes and other selected raw materials.

The wear resistance of the resulting glass-ceramics produced from both slate waste and copper mill tailings was measured and shown to be better than that of a 45-pct- $\text{Al}_2\text{O}_3$  ceramic. Optimization of crystallite size and percent crystallinity of these glass-ceramics by varying

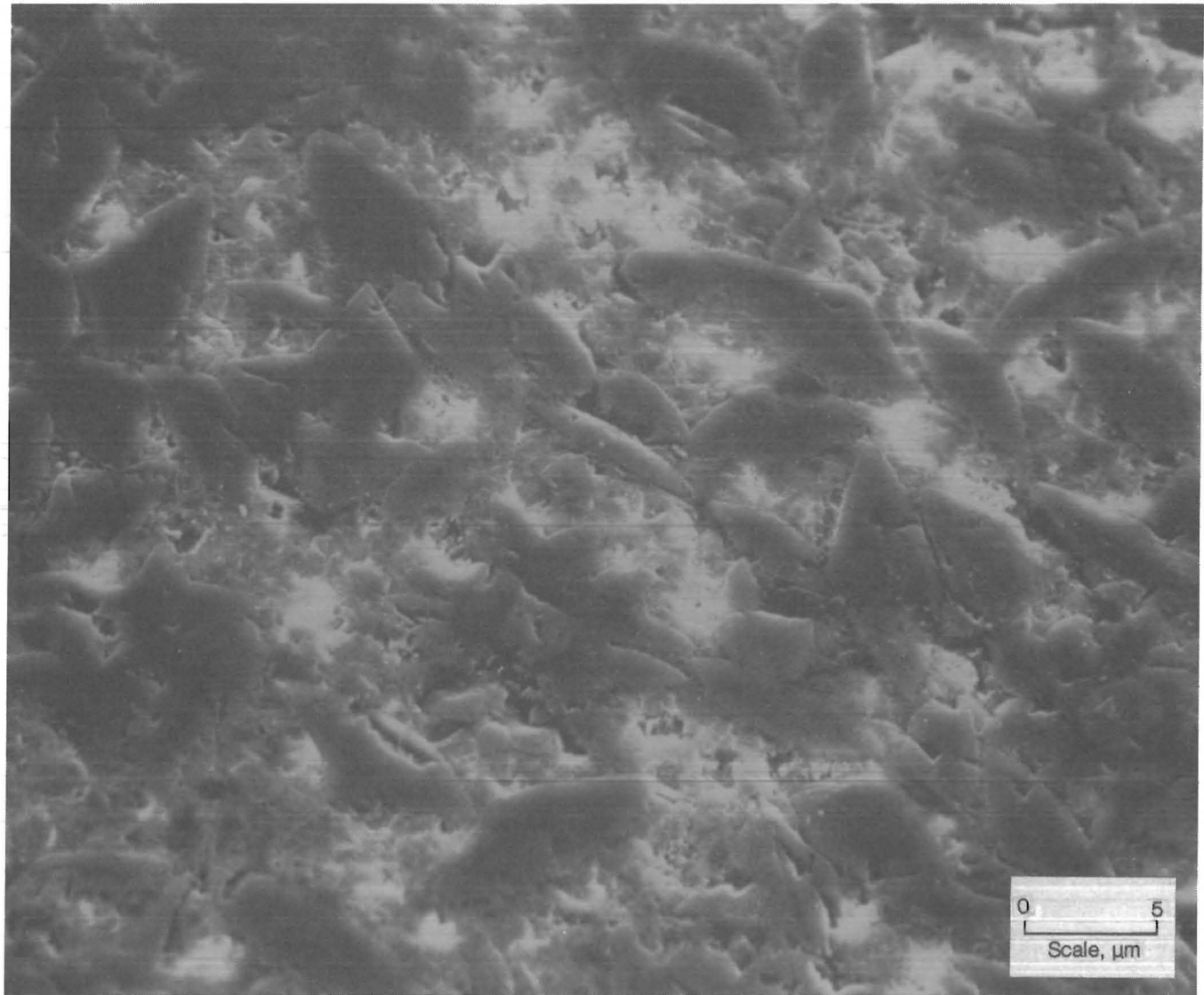


FIGURE 11. - Scanning electron micrograph of glass-ceramics produced from copper mine tailings.

the heat treatment cycle should result in higher wear-resistance values. These glass-ceramic materials could provide an

economical substitute for other ceramics and high-alloy steels presently used in high-wear applications.

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## APPENDIX A.--MINING AND PROCESSING WASTES

Basically, mining and processing waste materials can be divided into five categories:

1. Mining wastes--primarily waste rock and mill tailings.
2. Blast furnace and steelmaking slags.
3. Nonferrous slags from smelters.
4. Municipal incinerator wastes or other nonprocessed municipal wastes.
5. Byproducts from coal combustion.

#### MINING WASTES--PRIMARILY WASTE ROCK AND MILL TAILINGS

Mining waste (waste rock and mill tailings) by far accounts for the largest source of waste materials, with estimates of about 2.2 billion tons/yr (8).<sup>1</sup> Included in this group are mineral mining

wastes, primarily waste rock, mill tailings, and slimes. Table A-1 summarizes the annual quantities of these wastes produced by the various industries, as well as estimated accumulations. Obviously the physical and chemical characteristics of these wastes depend on their source and the method of processing. However, in general,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ , and  $\text{CaO}$ , all of which are basic components of raw materials used by the ceramic industry, constitute the bulk of most waste materials. Many of these wastes occur as carbonates, sulfates, or phosphates, resulting in considerable weight loss on heating to form the various oxides. Many of these wastes also contain various trace elements that are subject to leaching, thus creating environmental problems and limiting their use. The utilization of these wastes by the ceramic industry, in which high temperatures are used to bond or melt the materials, would in many cases eliminate or at least greatly reduce leaching. Thus, the potential exists for use of materials otherwise unsuitable for back-fill, landfill, soil conditioning, or soil stabilization.

<sup>1</sup>Underlined numbers in parentheses refer to items in the list of references preceding this appendix.

TABLE A-1. - Amounts of major mining wastes, million tons

Mining industry	Waste rock per year <sup>1</sup>	Process waste per year	Estimated accumulated process waste
Asbestos.....	0.6	2	14
Barite.....	1.9	3.1	24
Coal.....	NA	100	3,000
Copper.....	624	234	7,700
Dredge spoil.....	270-360	NAp	Uncertain
Feldspar.....	.2	.8	Uncertain
Fluorspar.....	.1	.4	Uncertain
Gold.....	15	5	450
Gypsum.....	14.2	2.7	Uncertain
Iron ore.....	27	27	800
Lead.....	.5	8	180
Phosphate.....	230	<sup>2</sup> 54	<sup>3</sup> 907
Quarry.....	68	NAp	Uncertain
Taconite.....	100	109	4,000
Uranium.....	156	5.8	110
Zinc.....	.9	7.2	180

NA Not available. NAp Not applicable.

<sup>1</sup>Includes overburden in some cases.

<sup>2</sup>Includes both phosphate slimes and phosphogypsum.

<sup>3</sup>Includes estimated 136 billion tons of phosphogypsum.

One of the large single sources of mining waste is coal refuse. Current annual generation is in excess of 100 million tons, with total accumulations of over 3.0 billion tons. As energy demands move toward a greater utilization of coal, these figures will increase dramatically. These wastes are composed primarily of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Fe}_2\text{O}_3$  and can be utilized by the ceramic industry.

#### BLAST FURNACE AND STEELMAKING SLAGS

Blast furnace and other ferrous slags, including converter and foundry slags, account for about 60 million tons annually. Traditionally, ferrous slags have been well utilized. There are several reasons for this, including a relatively constant supply of predictable size and composition, and concentration in certain geographic areas. In addition, ferrous slags are generated as molten material and with proper design can be converted into marketable form as they are drawn from the steel furnaces and processed, with minimal additional energy required. At present, approximately 80 pct of the ferrous slags are being used in this country, primarily to produce synthetic aggregate. However, most slags, if properly quenched, exhibit hydraulic properties and could be utilized as additives to cementitious materials having a much higher market value than aggregate.

#### NONFERROUS SLAGS

Approximately 10 million tons of nonferrous slags are produced each year at ore smelting and roasting facilities throughout the United States. Primary sources for these wastes are the copper, lead, nickel, phosphate, and zinc industries. Again,  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{MgO}$  are the major oxide components. Limited uses have been found for these slags in ceramic products, including roadway aggregate, cement replacement in backfill, portland cement, and calcium silicate brick. Drawbacks for their use include widely dispersed production, often in remote areas far from suitable

markets; the high density of the materials, making transportation expensive; and the fact that many contain valuable trace elements, prompting producers to stockpile them for recovery when the technology becomes available or economic incentives become a factor.

#### MUNICIPAL WASTES

Municipal incinerator wastes and other nonprocessed municipal wastes have received attention primarily as highway construction materials. The potential of recycling glass from systems designed to adequately separate municipal waste, or in areas where governmental regulations require separation by consumers, is of interest to the glass industry, which uses cullet in container or fiberglass production. Ground waste glass can be used as an additive to reduce the firing temperature of structural products such as brick and tile. Major problems, however, are the availability in quantity, the particle size of the glass, and the presence of organic material and soluble salts in waste glass recovered from municipal refuse (9).

#### BYPRODUCTS FROM COAL COMBUSTION

This category includes the byproducts of coal combustion, primarily fly ash, boiler slag, and bottom ash. Between 1965 and 1975 there was a twofold increase in the rate of generation, and an even greater growth is anticipated as coal gains impetus as an energy source. Although much research has been done on the utilization of the products of coal production, as recently as 1975 only 10 pct of the material produced found a market. Primarily this has been in the production of portland cement, as an admixture in concrete and bituminous products, in roofing, in the manufacture of lightweight aggregate, and in soil stabilization.

As with other wastes, the primary composition is  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ , and  $\text{MgO}$ . Also included is from 1 to 12 pct unburned carbon.

## APPENDIX B.--CENTRIFUGAL CASTING PROCESS

Anthony Eckard patented the centrifugal casting process in England in 1809 (10). Since that time various technological improvements have been made that facilitate the use of a variety of raw feed materials that are required in fabricating metal, concrete, and glass products.

A complete history of the development of centrifugal casting up to 1947 has been published by the American Foundrymen's Society (11). The publication also discusses many of the technological problems. In simplified terms, centrifugal casting employs horizontally positioned molds or slightly tilted mold arrangements that revolve about a longitudinal axis to impart the necessary centrifugal force to the mold. Material introduced to this revolving mold impinges on the inner surface of the mold and is shaped to the contours of the mold as a result of centrifugal force. Ideally, the theoretical centrifugal force on the mold is calculated using the following equation:

$$F = \frac{W}{g} \frac{4\pi^2 N^2 r}{12 \times 3,600}, \quad (B-1)$$

where  $F$  = centrifugal force, lbf,

$W$  = weight of the body, lbf,

$g$  = acceleration of gravity, 32.2 ft/s<sup>2</sup>,

$N$  = rotational speed, rpm,

and  $r$  = radius of the mold, in.

The force  $F$  does not have physical significance in the design of centrifugal casting procedures or equipment. Of greatest significance is the interfacial pressure between the mold and the liquid casting, as described by equation B-2 and represented in figure B-1.

$$P_i = \frac{\rho w t (r_m)^2 t}{(32.2) (12) r_i} \frac{N^2 (2\pi)^2}{60}, \quad (B-2)$$

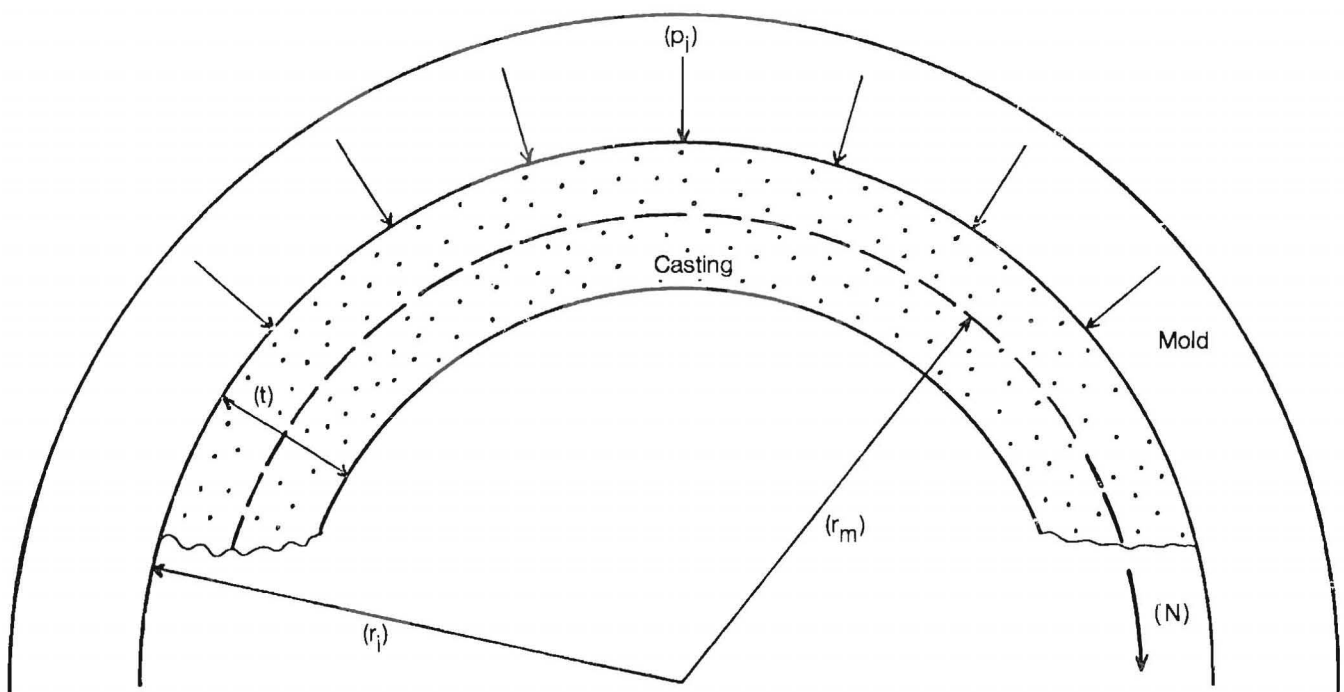


FIGURE B-1. - Stress element for centrifugal casting.

where  $p_i$  = interfacial pressure, lbf/in<sup>2</sup>,

$\rho_{wt}$  = weight per unit volume, lbf/in<sup>3</sup>,

$r_m$  = mean radius of casting, in,

$r_i$  = radius of mold-casting interface, in,

$t$  = thickness of casting, in,

and  $N$  = rotational speed, rpm.

Theoretical expressions are often used in determining minimal values. However, empirical expressions such as equation B-3 are generally used in practice (12).

$$N_m = \sqrt{\frac{265}{D}}, \quad (B-3)$$

where  $N_m$  = minimum number of revolutions per minute necessary to impart the required centrifugal force for a horizontal axis and pipe with a mean diameter,  $D$  (inches), to prevent the liquid from falling from the top of the mold during rotation.

Composition and viscosity of the melt and friction effects in the mold are taken into account in the constant term (265) of the equation.

#### CENTRIFUGAL CASTING OF METALS

To date, the principal application of centrifugal casting in the United States has been in the production of seamless metal pipe. Originally, molten iron, alloyed to give definite physical properties to the finished pipe, was used to produce "sand-cast" pipe. This allowed mass production of a serviceable, low-cost product without involving costly heat treatment. In recent years, stainless and alloy-steel pipe have been manufactured successfully using centrifugal casting techniques. Today, even composite pipe is being produced. Pipe manufactured by duplex casting, as it is known, generally consist of a two-layer

composition that is the result of casting an alloy as an outer shell followed by a second alloy that forms the inner zone of the pipe (13).

#### CENTRIFUGAL CASTING OF CONCRETES

The production of centrifugal-cast concrete pipe, although similar to the process of producing metal pipe, introduces some technical differences owing to the heterogeneous nature of the portland cement, sand, and gravel mixture. The raw material feed, the rotational speed of the mold, and spinning time must be carefully controlled to prevent segregation during casting. Previous work at the Tuscaloosa Research Center on the centrifugal casting of refractory castables is summarized in Bureau RI 8362 (14).

#### CENTRIFUGAL CASTING OF MOLTEN ROCK

Methods used for centrifugally forming cast iron and molten basalt pipe are closely related, differing mainly in the physical properties of the respective raw materials used and the subsequent heat treatments of the formed bodies.

Historically, stonecasting dates back to the year 1850 when basalt and other rocks were melted, and pipe, roofing tile, and road paver shapes were cast utilizing standard foundry practices.

By 1950 Soviet scientists suggested the possibility of forming ceramic shapes by centrifugal casting (15), and by 1952 researchers at Hradec Kralove, Czechoslovakia, mastered the technique of centrifugally casting pipe from basalt melts (16). By early 1960 the Soviets were using melts of basalt and diabase to centrifugally cast glass-ceramic pipe for slurry lines and for piping of abrasive materials (17).

In 1959 Soviet scientists claimed to have produced the world's first "true" glass-crystalline material, slag-sitalls (18-19), using metallurgical blast furnace slags. The compositions of the sitalls ranged from 50 to 65 pct slag,

20 to 40 pct silica sand, 0 to 12 pct clay with additions of up to 4.6 pct sodium sulfate, and 10 to 12 pct crystallization catalysts.

Slag-sitalls generally consist of from 60 to 70 pct crystalline matter, and the remainder is a glassy phase between the crystals (20). The size of the crystals usually does not exceed 1  $\mu\text{m}$ . Owing to their fine crystalline structure, sitalls exhibit remarkable physical and chemical properties. For example, they have a relatively high mechanical strength (bending strength is 43,000 to 50,000 psi) and resist chemical attack and erosion. In the U.S.S.R., tiles of slag-sitalls, used for floor coverings, have an expected service life of 30 to 45 yr. Sitalls are also used as chamber linings, conduits, and gutters in many chemical and industrial plants.

Lipovskii (21) showed that with basalt and slag castings the compressive strength and wear resistance of a body increased as the crystalline phases increased to an optimum value of about 85 pct. Mechanical properties of glass-crystalline bodies also depend upon the phase composition and structure. Ultimately, the melt composition, the degree of crystallization, and the rate of crystal growth greatly influence the strength and general nature of the ceramic body.

A considerable amount of research has been done in selecting nucleating agents for glass-ceramic bodies. A nucleating agent forms sites where crystal growth begins. An important requisite for a nucleating agent is that the "seed material" must have a slightly higher melting point than the components of the original melt, yet it must be soluble in the molten glass at the higher crystallizing temperatures. As nucleation nears completion, the fabricated body must be reheated to temperatures above the crystal nucleating temperature and maintained at this level to promote optimum crystal growth. Another important

characteristic of a good nucleating catalyst is its ability to be homogeneously dispersed in the melt and, upon cooling, to form a two-phase separation of submicroscopic crystalline particles (22). Among the most effective with slags are  $\text{TiO}_2$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{CaF}_2$ , and  $\text{Fe}_2\text{O}_3$  when used in amounts of up to 5 wt pct (23).

Equipment used to centrifugally cast glass-ceramic pipe in the U.S.S.R. and Czechoslovakia is very similar to that used in manufacturing cast iron and concrete pipe. Generally, the apparatus consists of a horizontally positioned mold, capable of revolving at from 0 to 2,500 rpm. Molten feed is normally introduced along the centered interior of the mold via a heated launder. The heated launder is used to maintain an uninterrupted flow of molten glass from the melting furnace to the mold's interior. As a result of centrifugal force during rotation, the molten glass impinges against the interior of the mold. With apparatus of this type, pipe having a diameter from 8 to 16 in with a wall thickness of 1 in and a length of 3 ft 4 in have been produced in the U.S.S.R. (20).

In the Soviet operation, the temperature in the working region of the furnace is held between 1,520° and 1,560° C. The melt is transferred to a rotating, preheated mold, the speed of which depends on the diameter of the pipe being cast. Forming the pipe in this process takes about 40 s. Castings are hardened and crystallized in 5 to 6 min, and after the mold is removed from the centrifuge machine, the crystallized casting is hydraulically ejected.

Heat treatment is conducted in a tunnel kiln where pipe is heated to 860° to 880° C, held for several hours to allow further crystallization to occur, and then slowly cooled to anneal the devitrified pipe. The total heat treatment cycle requires from 20 to 24 h.



APPENDIX C.--COMPUTER PROGRAM TO OPTIMIZE MIXES OF WASTE MATERIALS  
FOR GLASS-CERAMIC COMPOSITIONS

```

100 DIM A(6,7),X(8),Y(8),K(8),Z(6),X$(8),B(8,6),Z$(6),Y1(8)
110 PRINT "WASTE PROGRAM":M=5
170 D=M+1:REM ALLOWS FOR "OTHERS"
180 FOR I=1 TO 6
185 FOR J=1 TO 8
190 B(J,I) = 0
195 NEXT J
197 NEXT I
200 GOSUB 8500:REM GETS NAMES OF OTHERS (1-3) - RETURNS WITH N2= # OF NAMED OTHERS
    (1-2) AND D=TOTAL # OF CATEGORIES
300 GOSUB 1000:REM GET ADDITIVES (MAKE UP) AND WEIGHTS
400 GOSUB 2000:REM GET PRIME WASTE PARAMETERS AND DESIRED MIX
500 GOSUB 3500:CALCULATE A-MATRIX
600 GOSUB 5000:REM SOLVE EQUATIONS
700 IF E=1 THEN 995
701 FOR I = 1 TO N
702 IF Z(I)>0 THEN 704
703 GOTO 4000
704 NEXT I
705 W1=0
710 FOR I=1 TO D
720 Y1(I) = X(I)
730 FOR J= 1 TO N
740 Y1(I) = Y1(I)+B(I,J)*Z(J)
750 NEXT J
760 W1=W1+Y1(I)
770 NEXT I
780 FOR I=1 TO D
785 Y1(I) = Y1(I)/W1
790 NEXT I
792 FOR I1=N+1-N1 TO N
794 STR(Z$(I1),13)="--->"
795 NEXT I1
796 PRINT "DO YOU WANT A PRINTOUT? ";
797 INPUT A$
798 IF A$="N" THEN 800
799 GOSUB 4100
800 PRINT "ANALYSIS CALLS FOR ADDING THE FOLLOWING PER 100 LBS OF WASTE"
810 PRINT Z$(1);100*Z(1),
815 IF N<2 THEN 855
820 PRINT Z$(2);100*Z(2)
825 IF N<3 THEN 860
830 PRINT Z$(3);100*Z(3),
835 IF N<4 THEN 855
840 PRINT Z$(4);100*Z(4)
845 IF N<5 THEN 860
850 PRINT Z$(5);100*Z(5),
852 IF N<6 THEN 855
853 PRINT Z$(6):GOTO 860
855 PRINT
860 PRINT "THIS YIELDS THE FOLLOWING MIX:"
870 PRINT "BASE ELEMENT", "ORIG. FRAC.", "DES. FRAC.", "FINAL FRAC."

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```

873  Y9=0
875  FOR I=1 TO D-1
876  Y9=Y9+Y1(I)
877  NEXT I
880  FOR I=1 TO D-1
890  PRINT X$(I),X(I),Y(I),Y1(I)/Y9
900  NEXT I
905  GOSUB 4200
910  END
995  PRINT "SOLUTION IS NOT UNIQUE. TRY A DIFFERENT WEIGHTING"
999  END
1000 PRINT "DO YOU WANT TO CONSIDER ALL OF THE FOLLOWING AVAILABLE?"
1010 PRINT "  1. SAND"
1020 PRINT "  2. CALCIUM CARBONATE"
1030 PRINT "  3. DOLOMITE"
1040 PRINT "  4. OTHERS (UP TO 3)"
1050 PRINT :PRINT "IF SO, ENTER 'Y' AND THE NAME AND MAKEUP OF 'OTHER' WHEN"
1060 PRINT "PROMPTED. IF NOT, ENTER 'N' AND INDICATE WHICH YOU WANT."
1070 PRINT :PRINT "ALL OF THE ABOVE (Y/N)";
1080 INPUT A$
1090 IF A$="Y" THEN 1500
1100 IF A$="N" THEN 1115
1110 GOTO 1000
1115 I=0
1120 PRINT "SAND (Y/N)";:INPUT S$
1123 IF S$="N" THEN 1130
1127 I=I+1:GOSUB 1510
1130 PRINT "CALCIUM CARBONATE (Y/N)";:INPUT C$
1133 IF C$="N" THEN 1140
1137 I=I+1:GOSUB 1530
1140 PRINT "DOLOMITE (Y/N)";:INPUT D$
1143 IF D$="N" THEN 1150
1147 I=I+1:GOSUB 1550
1150 PRINT "OTHERS (Y/N)";:INPUT O$
1160 IF O$ = "N" THEN 1230
1161 PRINT "HOW MANY OTHERS? (1-3)"
1162 INPUT N1
1163 N=I+1:REM # OF 1st 'OTHER'
1164 FOR I1=1 TO N1
1165 PRINT "NAME OF OTHER#";I1;"-->";:INPUT Z$(I+I1)
1166 NEXT I1
1170 FOR I1=N TO I+N1
1171 PRINT "IS THE MAKEUP IN THE DATA BASE FOR ";Z$(I1);"? (Y/N)";
1172 INPUT A$:IF A$="N" THEN 1179
1173 GOSUB 3000
1174 FOR I2=1 TO D
1175 B(I2,I1) = X(I2)
1176 NEXT I2
1177 GOTO 1225
1178 NEXT I1: GOTO 1230
1179 PRINT "WHAT ARE THE COMPONENTS OF THIS 'OTHER ADDITIVE'?"
1180 PRINT "% SI BASED";:INPUT B(1,I1):B(1,I1)=B(1,I1)/100
1190 PRINT "% CA BASED";:INPUT B(2,I1):B(2,I1)=B(2,I1)/100
1200 PRINT "% MG BASED";:INPUT B(3,I1):B(3,I1)=B(3,I1)/100
1202 PRINT "% AL BASED";:INPUT B(4,I1):B(4,I1)=B(4,I1)/100

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1206 PRINT "% FE BASED";:INPUT B(5,I1):B(5,I1)=B(5,I1)/100
1207 IF N2=0 THEN 1210
1208 FOR I2=1 TO N2:PRINT "% BASED ON ";X$(M+I2)
1209 INPUT B(M+I2,I1):B(M+I2,I1)=B(M+I2,I1)/100:NEXT I2
1210 B(D,I1)=1:FOR I2=1 TO M+N2:B(D,I1)=B(D,I1)-B(I2,I1):NEXT I2
1215 IF B(D,I1)>=0 THEN 1220
1216 PRINT "LEAVES 'OTHER' < 0%! REENTER"
1217 GOTO 1179
1220 PRINT "OTHER ELEMENTS MAKE UP ";100*B(D,I1);"%"
1225 NEXT I1
1230 N=I+N1:REM NUMBER OF ADDITIVES
1240 PRINT "EQUAL WEIGHT FOR EACH PERCENTAGE DIFFERENCE (Y/N)";
1250 INPUT A$
1260 IF A$="Y" THEN 9000
1270 IF A$="N" THEN 9050
1280 GOTO 1240
1500 S$="Y":D$="Y":O$="Y"
1502 I=1:GOSUB 1510
1504 I=2:GOSUB 1530
1506 I=3:GOSUB 1550
1507 I=3: GOTO 1161
1508 I=4:Z$(4)="OTHER      -->"
1509 GOTO 1170
1510 Z$(I)="SAND      -->":B(1,I)=1
1520 B(2,I)=0:B(3,I)=0:B(4,I)=0:B(5,I)=0:B(6,I)=0
1525 RETURN
1530 Z$(I)="CALC. CARB. -->":B(2,I)=.56
1540 B(1,I)=0:B(3,I)=0:B(4,I)=0:B(5,I)=0:B(6,I)=0
1545 RETURN
1550 Z$(I)="DOLOMITE  -->"
1560 B(2,I)=.304:B(3,I)=.218
1565 RETURN
2000 T=0:REM ** GET PARAMETERS **
2002 PRINT "NOW WE NEED THE 'PRIME' WASTE MAKEUP"
2005 PRINT "GET THE MAKE-UP FROM DATA BASE (Y/N)";:INPUT A$
2006 IF A$="N" THEN 2010
2007 GOSUB 3000
2008 GOTO 2100
2010 FOR I = 1 TO M+N2
2020 PRINT "WHAT PERCENT OF THE WASTE IS ";X$(I);
2030 INPUT X(I)
2040 X(I) = X(I)/100
2050 T=T+X(I)
2060 NEXT I
2070 IF T>1 THEN 2090
2080 X(D)=1-T:PRINT "OTHER IS ";100*X(D);" %." :GOTO 2100
2090 PRINT "TOTAL > 100% - RETRY ":GOTO 2000
2100 P=0: FOR I = 1 TO M+N2
2110 PRINT "WHAT PERCENT OF THE FINISHED PRODUCT SHOULD BE ";X$(I);
2120 INPUT Y(I)
2130 Y(I) = Y(I)/100
2140 P=P+Y(I)
2150 NEXT I
2160 IF P>1 THEN 2190
2170 Y(D) = 1-P

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2180 PRINT "AND OTHER IS TO BE ";100*Y(D);" % ":RETURN
2190 PRINT "TOTAL > 100% - RETRY ":GOTO 2100
3000 REM **GET MAKEUP FROM DISC**
3005 PRINT "DATA BASE WILL GIVE PERCENTAGE OF SIO2, CAO, MGO, AL2O3 & FE2O3"
3006 PRINT "IF YOU HAVE NAMED SOME 'OTHER' CATEGORIES, IT WILL REQUIRE YOU"
3007 PRINT "TO ENTER THEIR DATA FROM THE KEYBOARD. READY? (Y/N)";
3008 INPUT A$:IF A$="Y" THEN 3010
3009 PRINT "WANT TO QUIT? (Y/N) ":INPUT A$:IF A$="N"THEN 3005:END
3010 PRINT "CHECK ON WHICH WASTE?"
3020 PRINT " 1. TACONITE TAILINGS          15. FOUNDRY SLAG"
3030 PRINT " 2. COPPER TAILINGS          16. COPPER SLAG"
3040 PRINT " 3. GOLD TAILINGS              17. FERROMOLYBDNUM SLAG"
3050 PRINT " 4. LEAD-ZINC TAILINGS         18. TIN SLAG"
3060 PRINT " 5. RED MUD                    19. PHOSPHATE SLAG"
3070 PRINT " 6. BROWN MUD                  20. LEAD SLAG"
3080 PRINT " 7. PHOSPHATE SLIME             21. NICKEL SLAG"
3090 PRINT " 8. CEMENT KILN DUST           22. ZINC SLAG"
3100 PRINT " 9. ANTHRACITE COAL REFUSE     23. MUNICIPAL RECOVERY RESIDUE"
3110 PRINT "10. BITUMINOUS COAL REFUSE     24. BITUMINOUS FLY ASH"
3120 PRINT "11. BLAST FURNACE SLAG         25. LIGNITE FLY ASH"
3130 PRINT "12. BOF STEEL SLAG               26. ANTHRACITE FLY ASH"
3140 PRINT "13. OPEN HEARTH SLAG            27. BOTTOM ASH"
3150 PRINT "14. CONVERTER SLAG              28. BOILER SLAG"
3160 PRINT "ENTER YOU CHOICE OR '0' FOR NONE-OF-THE-ABOVE." ;:INPUT N4
3170 IF N4>0 THEN 3200
3171 IF N4<0 THEN 3010
3175 PRINT "29. SLATE WASTE"
3176 PRINT "30. COPPER MILL TAILINGS"
3177 PRINT "31. SERPENTINE"
3178 PRINT "32. CANCEL DATA BASE SEEK"
3179 PRINT "ENTER -1 TO RETURN TO BEGINNING OF LIST"
3180 GOTO 3160
3190 PRINT "THAT'S ALL WE'VE GOT. RUN PROGRAM AGAIN TO ENTER YOUR OWN":END
3200 IF N4<32 THEN 3220
3205 PRINT "TRY AGAIN ENTERING YOUR OWN WASTE MAKEUP":END
3210 GOTO 3000
3220 DATA LOAD DC OPEN F "DATFIL"
3230 N5=N4-1
3240 IF N5=0 THEN 3260
3250 DSKIP N5
3260 DATA LOAD DC X$,X(1),X(2),X(3),X(4),X(5)
3262 X(6)=100-X(1)-X(2)-X(3)-X(4)-X(5)
3270 PRINT "IS ";X$;" CORRECT (Y/N)";:INPUT A$
3280 IF A$="N" THEN 3000
3290 IF N2=0 THEN 3330
3300 FOR I3=1 TO N2
3310 PRINT "WHAT PERCENT OF THE WASTE IS ";X$(M+I3);" --> ";
3320 INPUT X(M+I3): NEXT I3
3330 X(D)=100:FOR I3=1 TO D-1:X(D)=X(D)-X(I3):NEXT I3
3340 IF X(D)<0 THEN 2090
3350 FOR I3=1 TO D: X(I3)=X(I3)/100: NEXT I3
3499 RETURN
3500 REM **CALCULATE MATRIX COEFFICIENTS**
3510 FOR K=1 TO N
3520 FOR I=K TO N

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3530 A(K,I)=0
3540 FOR J=1 TO D
3550 A(K,I) = A(K,I)+K(J)*(B(J,I)-Y(J))*(B(J,K)-Y(J))
3560 NEXT J
3570 A(I,K)=A(K,I)
3580 NEXT I
3590 A(K,N+1) = 0
3600 FOR J=1 TO D
3610 A(K,N+1) = A(K,N+1)+K(J)*(X(J)-Y(J))*(Y(J)-B(J,K))
3620 NEXT J
3630 NEXT K
3999 RETURN
4000 PRINT "NEGATIVE QUANTITIES ARE PRESENT"
4010 PRINT "WANT A PRINTOUT ANYWAY (Y/N)";
4020 INPUT A$
4030 IF A$="Y" THEN 705
4040 PRINT "WANT TO TRY SOMETHING ELSE";
4050 INPUT A$
4060 IF A$="Y" THEN 110
4070 END
4100 SELECT PRINT 215
4110 RETURN
4200 SELECT PRINT 005
4210 RETURN
5000 REM *****
5010 REM *
5020 REM *      GAUSS-JORDAN INVERSION      *
5030 REM * REQUIRES N (NUMBER OF VARIABLES) *
5040 REM * A(N,N+1) AUGMENTED MATRIX COEFF. *
5050 REM *      RETURNS Z(N) - SOLUTIONS      *
5060 REM * IF E=1 ON RETURN, NO UNIQUE SOLN *
5070 REM *
5080 REM *****
5200 E=0 : REM ERROR FLAG
5210 FOR S=1 TO N
5220 FOR T=S TO N
5230 IF A(T,S)<>0 THEN 5240
5235 NEXT T
5237 E=1
5238 GOTO 5999
5240 GOSUB 5510
5250 C=1/A(S,S)
5260 GOSUB 5610
5270 FOR T=1 TO N
5275 IF T=S THEN 5300
5280 C=-A(T,S)
5290 GOSUB 5710
5300 NEXT T
5305 NEXT S
5310 GOTO 5800
5510 FOR J=1 TO N+1
5520 B=A(S,J)
5530 A(S,J)=A(T,J)
5540 A(T,J)=B
5550 NEXT J

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5560 RETURN
5610 FOR J=1 TO N+1
5620 A(S,J)=C*A(S,J)
5630 NEXT J
5640 RETURN
5710 FOR J=1 TO N+1
5720 A(T,J)=A(T,J)+C*A(S,J)
5730 NEXT J
5740 RETURN
5800 FOR T=N TO 1 STEP -1
5810 Z(T) = A(T,N+1)
5820 IF T=N THEN 5860
5830 FOR J=1 TO N-T
5840 Z(T)=Z(T)-A(T,T+J)*A(T+J,N+1)
5850 NEXT J
5860 NEXT T
5999 RETURN
8000 PRINT "IT IS NOW TIME TO ENTER THE NAME OF THE COMPONENTS."
8010 PRINT "LIST FIRST THOSE COMPONENTS WHICH CAN BE ADDED TO THE MIX."
8020 PRINT "THE LAST ENTRY IS AUTOMATICALLY 'OTHERS'."
8040 FOR I=1 TO M
8050 PRINT "WHAT IS THE NAME OF COMPOUND #";I;
8060 INPUT X$(I)
8080 NEXT I
8090 X$(D) = "OTHER"
8099 RETURN
8500 X$(1) = "SIO2"
8510 X$(2) = "CAO"
8520 X$(3) = "MGO"
8530 X$(4) = "AL2O3"
8540 X$(5) = "FE2O3"
8550 PRINT "HOW MANY IMPORTANT CONSTITUENTS ARE TO BE ACCOUNTED FOR IN ADDITION TO
      SIO2, CAO, MGO, AL2O3 AND FE2O3? YOU MAY HAVE";
8555 PRINT "FROM 0 TO 2 ADDITIONAL NAMED CONSTITUENTS PLUS THE CATCHALL CATEGORY
      OF 'OTHER' WHICH INCLUDES THE REMAINDER. (0-2)"
8560 INPUT N2
8570 IF N2<0 THEN 8550
8575 IF N2>2 THEN 8550
8580 IF N2=0 THEN 8630
8590 FOR I1=1 TO N2
8600 PRINT "NAME FOR ADDITIONAL CONSTITUENT #";I1
8610 INPUT X$(5+I1)
8620 NEXT I1
8630 X$(6+N2) = "OTHER"
8640 D=M+N2+1:REM TOTAL # OF CATEGORIES (6-8 DEPENDING ON N2)
8650 RETURN
9000 FOR I = 1 TO D
9010 K(I) = 1
9020 NEXT I
9030 RETURN
9050 FOR I = 1 TO D
9060 PRINT "RELATIVE IMPORTANCE OF ";X$(I); " -> ";
9070 INPUT K(I)
9080 NEXT I
9090 RETURN

```

## SAMPLE OUTPUT

:RUN

WASTE PROGRAM

HOW MANY IMPORTANT CONSTITUENTS ARE TO BE ACCOUNTED FOR IN ADDITION TO  $\text{SiO}_2$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$  AND  $\text{Fe}_2\text{O}_3$ ? YOU MAY HAVE FROM 0 TO 2 ADDITIONAL NAMED CONSTITUENTS PLUS THE CATCHALL CATEGORY OF 'OTHER' WHICH INCLUDES THE REMAINDER. (0-2)

? 2

NAME FOR ADDITIONAL CONSTITUENT # 1

? ALKALI

NAME FOR ADDITIONAL CONSTITUENT # 2

?  $\text{Cr}_2\text{O}_3$

DO YOU WANT TO CONSIDER ALL OF THE FOLLOWING AVAILABLE?

1. SAND
2. CALCIUM CARBONATE
3. DOLOMITE
4. OTHERS (UP TO 3)

IF SO, ENTER 'Y' AND THE NAME AND MAKEUP OF 'OTHER' WHEN PROMPTED. IF NOT, ENTER 'N' AND INDICATE WHICH YOU WANT.

ALL OF THE ABOVE (Y/N)? N

SAND (Y/N)? N

CALCIUM CARBONATE (Y/N)? Y

DOLOMITE (Y/N)? N

OTHERS (Y/N)? Y

HOW MANY OTHERS? (1-3)

? 3

NAME OF OTHER#1 -->?  $\text{MgO}$

NAME OF OTHER#2 -->?  $\text{Na}_2\text{CO}_3$

NAME OF OTHER#3 -->? CHROMITE

IS THE MAKEUP IN THE DATA BASE FOR  $\text{MgO}$ ? (Y/N)? N

WHAT ARE THE COMPONENTS OF THIS 'OTHER ADDITIVE'?

% SI BASED? 0

% CA BASED? 0

% MG BASED? 100

% AL BASED? 0

% FE BASED? 0

% BASED ON ALKALI

? 0

% BASED ON  $\text{Cr}_2\text{O}_3$

? 0

OTHER ELEMENTS MAKE UP 0 %

IS THE MAKEUP IN THE DATA BASE FOR  $\text{Na}_2\text{O}_3$ ? (Y/N)? N

WHAT ARE THE COMPONENTS OF THIS 'OTHER ADDITIVE'?

% SI BASED? 0

% CA BASED? 0

% MG BASED? 0

% AL BASED? 0

% FE BASED? 0

% BASED ON ALKALI

? 58.5

% BASED ON CR2O3

? 0

OTHER ELEMENTS MAKE UP 41.5%

IS THE MAKE UP IN THE DATA BASE FOR CHROMITE? (Y/N)? N

WHAT ARE THE COMPONENTS OF THIS 'OTHER ADDITIVE'?

% SI BASED? 1.9

% CA BASED? .2

% MG BASED? 11.9

% AL BASED? 17.2

% FE BASED? 23.3

% BASED ON ALKALI

? 0

% BASED ON CR2O3

? 43

OTHER ELEMENTS MAKE UP 2.5 %

EQUAL WEIGHT FOR EACH PERCENTAGE DIFFERENCE (Y/N)? N

RELATIVE IMPORTANCE OF SIO2 -> ? 1

RELATIVE IMPORTANCE OF CAO -> ? 1

RELATIVE IMPORTANCE OF MGO -> ? 1

RELATIVE IMPORTANCE OF AL2O3 -> ? 1

RELATIVE IMPORTANCE OF FE2O3 -> ? 1

RELATIVE IMPORTANCE OF ALKALI -> ? 10

RELATIVE IMPORTANCE OF CR2O3 -> ? 10

RELATIVE IMPORTANCE OF OTHER -> ? .1

NOW WE NEED THE 'PRIME' WASTE MAKEUP

GET THE MAKE-UP FROM DATA BASE (Y/N)? Y

DATA BASE WILL GIVE PERCENTGE OF SIO2, CAO, MGO, AL2O3 & FE2O3

IF YOU HAVE NAMED SOME 'OTHER' CATEGORIES, IT WILL REQUIRE YOU

TO ENTER THEIR DATA FROM THE KEYBOARD. READY? (Y/N) ? Y Y

CHECK ON WHICH WASTE?

- |                            |                                |
|----------------------------|--------------------------------|
| 1. TACONITE TAILINGS       | 15. FOUNDRY SLAG               |
| 2. COPPER TAILINGS         | 16. COPPER SLAG                |
| 3. GOLD TAILINGS           | 17. FERROMOLYBDNUM SLAG        |
| 4. LEAD-ZINC TAILINGS      | 18. TIN SLAG                   |
| 5. RED MUD                 | 19. PHOSPHATE SLAG             |
| 6. BROWN MUD               | 20. LEAD SLAG                  |
| 7. PHOSPHATE SLIME         | 21. NICKEL SLAG                |
| 8. CEMENT KILN DUST        | 22. ZINC SLAG                  |
| 9. ANTHRACITE COAL REFUSE  | 23. MUNICIPAL RECOVERY RESIDUE |
| 10. BITUMINOUS COAL REFUSE | 24. BITUMINOUS FLY ASH         |
| 11. BLAST FURNACE SLAG     | 25. LIGNITE FLY ASH            |
| 12. BOF STEEL SLAG         | 26. ANTHRACITE FLY ASH         |
| 13. OPEN EARTH SLAG        | 27. BOTTOM SLAG                |
| 14. CONVERTER SLAG         | 28. BOILER SLAG                |

ENTER YOU CHOISE OR '0' FOR NONE-OF-THE-ABOVE.? 0

29. SLATE WASTE

30. COPPER MILL TAILINGS

31. SERPENTINE

32. CANCEL DATA BASE SEEK

ENTER -1 TO RETURN TO BEGINNING OF LIST

ENTER YOUR CHOICE OR '0' FOR NONE-OF-THE-ABOVE.? 29

IS SLATE WASTE CORRECT (Y/N)? Y

WHAT PERCENT OF THE WASTE IS ALKALI --> ? 4.15

WHAT PERCENT OF THE WASTE IS CR2O3 --> ? 0

WHAT PERCENT OF THE FINISHED PRODUCT SHOULD BE SIO<sub>2</sub>? 48  
 WHAT PERCENT OF THE FINISHED PRODUCT SHOULD BE CAO? 17.6  
 WHAT PERCENT OF THE FINISHED PRODUCT SHOULD BE MGO? 6.8  
 WHAT PERCENT OF THE FINISHED PRODUCT SHOULD BE AL<sub>2</sub>O<sub>3</sub>? 13.5  
 WHAT PERCENT OF THE FINISHED PRODUCT SHOULD BE FE<sub>2</sub>O<sub>3</sub>? 5.1  
 WHAT PERCENT OF THE FINISHED PRODUCT SHOULD BE ALKALI? 6.5  
 WHAT PERCENT OF THE FINISHED PRODUCT SHOULD BE CR<sub>2</sub>O<sub>3</sub>? 2.5  
 AND OTHER IS TO BE 0 %

DO YOU WANT A PRINTOUT? ? Y

ANALYSIS CALLS FOR ADDING THE FOLLOWING PER 100 LBS OF WASTE

CALC. CARB. --> 24.36060618668 MGO --> 2.269027333109

NA<sub>2</sub>CO<sub>3</sub> --> 6.484442821291 CHROMITE --> 5.648697076579

THIS YIELDS THE FOLLOWING MIX:

BASE ELEMENT	ORIG. FRAC.	DES. FRAC.	FINAL FRAC.
SIO <sub>2</sub>	.617	.48	.5442613667781
CAO	6.00000000E-03	.176	.1255107892639
MGO	8.00000000E-03	6.80000000E-02	3.29443596E-02
AL <sub>2</sub> O <sub>3</sub>	.162	.135	.1512090246677
FE <sub>2</sub> O <sub>3</sub>	4.90000000E-02	5.10000000E-02	5.47379834E-02
ALKALI	4.15000000E-02	6.50000000E-02	6.99477805E-02
CR <sub>2</sub> O <sub>3</sub>	0	2.50000000E-02	2.13886955E-02

END PROGRAM

FREE SPACE=1135